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Box Patent Application

Sir:

Transmitted herewith for filing is the patent application of

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Schmidt, Peter F. McGarry, Jean-Pierre Wolf and Randall B. Nelson

For: **INHIBITION OF PULP AND PAPER YELLOWING USING
HYDROXYLAMINES AND OTHER COADDITIVES**

Enclosed are:

- ☒ 27 pages of specification including claims
- ☒ 1 page(s) of abstract
- ☐ ___ sheet(s) of drawing ☐ formal ☐ informal
- ☐ Executed Declaration and Power of Attorney (original)
- ☐ Declaration and Power of Attorney (copy) (For continuations/divisionals)
- ☐ Associate Power of Attorney
- ☐ Preliminary Amendment
- ☒ This application is a ☒ continuation-in-part of prior application No. 09/177,016 filed on
October 22, 1998.

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INHIBITION OF PULP AND PAPER YELLOWING
USING HYDROXYLAMINES AND OTHER COADDITIVES

This is a continuation-in-part of application Serial No. 09/177,016, filed on October 22, 1998.

The instant invention pertains to a method for preventing the loss of brightness and for enhancing resistance to yellowing in pulp or paper, particularly pulp or paper which still contains lignin, by the addition of N,N-dialkylhydroxylamines, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine, or their salts and other coadditives.

Background of the Invention

High-yield and ultra-high yield wood pulps undergo rapid light-induced discoloration, particularly when they are exposed to near ultraviolet light (wave lengths 300-400 nm) in indoor fluorescent light and daylight. This characteristic restricts their use to short-life, low-value paper products. High-yield and ultra-high yield wood pulps can be bleached to a high level of whiteness. If this whiteness could be stabilized against discoloration, these bleached high-yield pulps could displace significant amounts of more expensive fully-bleached, low-yield chemical pulps.

This discoloration is ascribed to the substantial lignin content of high-yield pulps totally about 20-30% by mass. Phenoxy radicals are the key intermediates in the reaction mechanism. Several light-induced reactions have been proposed to account for their formation such as cleavage of the aryl ether bond of phenacyl aryl ether groups, or breakdown of ketyl radicals formed from saturated aryl-glycerol β -aryl ether structures in lignin. The phenoxy radicals are oxidized by other oxygen-centered radicals (alkoxy and perhydroxy) to form yellow chromophores.

I. E. Arzkin et al., Khimiya drevesiny (Chemistry of Wood), 1982, No. 2, 114 and A. D. Sergeev et al., *ibid*, 1984, No. 5, 20 disclosed that the use of iminoxyl radicals such as TEMPO (1-oxyl-2,2,6,6-tetramethylpiperidine) is useful in the delignification of wood using the one-stage oxygen-soda (alkaline) process, but made no mention or suggestion of any activity provided by TEMPO on preventing light-induced discoloration of paper or pulp made from such treated wood.

V. I. Khodyrev et al., Vysokomol soyed, A29, No. 3, 616 (1987) [Polymer Sci. U.S.S.R., 29, No. 3, 688 (1987)] show that the photoinitiated oxidation by oxygen causes weathering of cellulosic textile materials such as flax or cotton, and that the light stability of the cellulose could be improved by photostabilizers such as the UV absorbers, benzophenols and 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine. The UV absorbers offer no protection, and are actually detrimental. The authors noted that the stable nitroxyl radical interacts with alkyl radicals in the cellulose to afford its salubrious stabilizing activity. There is no suggestion by the authors that this stabilizing activity could be applied successfully in wood pulp and/or paper made therefrom.

M-K. Syler et al., J. Assn. Paper Pulp Tech, 29, 135 (1990) show that selected metal salts such as magnesium sulfate and lower alkanolic acids inhibit color reversion in bleached pulp.

P. Fournier de Violet et al., Cellulose Chem. Tech., 24, 225 (1990) show that the use of UV absorbers and hydrogen donor agents such as thiols, ascorbic acid, etc. help prevent the photoinduced discoloration of hydrogen peroxide bleached wood pulp, but that chain breakers such as hindered phenols and hindered amines (having >N-H or >N-CH₂-moieties) had no or even a detrimental effect on preventing photoinduced discoloration.

R. Agnemo et al., 6th International Symposium on Wood and Pulp Chemistry, Appita, 1991, confirmed that free hydroxyl radicals plus lignin lead to undesirable photoyellowing in pulp and paper.

S. Omori et al., J. Assn. Paper Pulp Tech, 48, 1388 (1993) describes the effect of antioxidants and UV absorbers on light reversion and concludes that the combination of an antioxidant and UV absorber prevents color reversion and has a synergistic effect in that activity.

M. Paulsson et al., 8th International Symposium Wood and Pulping Chemistry, Helsinki, 1995, show that efficient photostabilization of unbleached paper or hydrogen peroxide bleached TMP pulp can be achieved by acetylation.

There have been a number of different approaches proposed to inhibiting the yellowing of mechanical pulps. These include: radical scavengers and antioxidants; UV screens; elimination of chromophores after their formation; chemical modification of lignin by alkylation or acetylation; polymeric inhibitors; and two types of coadditives used in combination. Z-H. Wu et al., *Holzforschung*, 48, (1994), 400 discuss the use of radical scavengers like phenyl-N-tert-butyl nitron to reduce the formation of chromophores during mechanical pulping and give a more light-stable pulp.

C. Heitner, Chemistry of Brightness Reversion and Its Control, Chapter 5, TAPPI, Atlanta, 1996, pp 183-211, summarizes the state of the art in the thermal and light-induced yellowing of lignin-containing pulps such as thermomechanical (TMP) and chemithermomechanical (CTMP) pulps, showing the seriousness of these undesirable effects discusses generally the then current prior art methods used to attack this problem. These include bleaching, the use of phosphites, UV absorbers, polyalkylene glycols and free radical scavengers such as ascorbic acid, thiols, thioethers, dienes and aliphatic aldehydes and chelating agents such as ethylenediaminetetraacetic acid (EDTA). The author concluded that, although much progress had been made, much still remains to be done before a successful and practical solution to this loss of brightness and undesirable yellowing of lignin-containing pulp and/or paper is found.

Copending application Serial No. 09/119,567 describes a potential solution where the use of selected hindered amine nitroxides, hindered amine hydroxylamines or their

salts in combination with selected UV absorbers and metal chelating agents is seen to prevent loss of brightness and to enhance resistance to yellowing in pulp or paper still containing lignin.

Canadian Patent Application No. 2,164,394 and WO 97/36041 teach a multi-component system for modifying, degrading or bleaching lignin-containing materials. This system includes an oxidation catalyst as an essential component. The catalysts are selected enzymes such as oxidoreductases of classes 1.1.1 to 1.97. The system also includes a number of mediators which inter alia include lower N,N-dialkylhydroxylamines and N,N-dibenzylhydroxylamine.

The instant invention describes another approach to this important problem where the use of N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine or their salts in combination with selected coadditives also prevents the loss of brightness and enhances resistance to yellowing in pulp or paper, especially pulp or paper still containing lignin. The ester, amide or thio substituted N,N-dialkylhydroxylamines are described in United States Patent Nos. 4,612,393; 4,720,517 and 5,019,285.

Detailed Description of the Invention

The addition of N,N-dialkylhydroxylamines, derivatives thereof or N,N-dibenzylhydroxylamine to high-yield pulp paper either alone or in combinations with UV absorbers, metal chelating agents, fluorescent whitening agents and/or stabilizing polymers effectively achieves light and thermal stability which is similar to that found in papers made from kraft pulps.

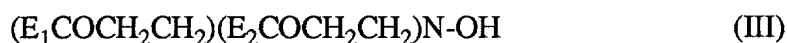
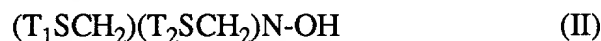
Hydroxylamines are known to be efficient free radical traps and may limit the production of o-quinones; UV absorbers limit photochemistry in the underlying substrate

to which they are applied, and ultimately reduce the production of free radicals. UV absorbers and hydroxylamines are each effective at stemming some of the free radical chemistry leading to paper yellowing when used singly. However, when they are used together, hydroxylamines and UV absorbers can act synergistically to effectively stop photochemical yellowing of lignin containing papers. The hydroxylamines show enhanced inhibiting activity when combined with a metal chelating agent such diethylenetriamine-pentaacetic acid or citric acid, or polymeric inhibitors such as polyethylene glycol.

More particularly, the instant invention pertains to a composition having enhanced resistance to yellowing which comprises

(a) a pulp or paper, especially a pulp or paper which still contains lignin, and

(b) an effective stabilizing amount of an N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine of formula I, II or III



where

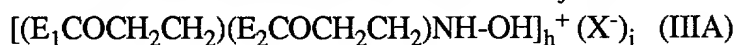
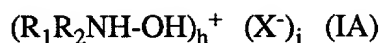
R_1 and R_2 are independently alkyl of 1 to 18 carbon atoms, alkyl of 1 to 18 carbon atoms substituted by a hydroxyl group; or benzyl;

T_1 and T_2 are independently alkyl of 1 to 4 carbon atoms, phenyl, 3,5-di-tert-butyl-4-hydroxyphenyl, benzyl or $-CH_2COOH$;

E_1 and E_2 are independently $-OE_3$, $-NHE_3$ or $-NE_3E_4$ where E_3 and E_4 are

independently hydrogen, alkyl of 1 to 4 carbon atoms or said alkyl substituted by one hydroxyl group; or

of an acid salt of formula IA, IIA or IIIA



where

X is an inorganic or organic anion, and

the total charge of cations h is equal to the total charge of anions j.

Preferably, X is phosphate, phosphonate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, gluconate, malate, mandelate, tiglate, ascorbate, polymethacrylate, a carboxylate of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, a diethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, an alkylsulfonate or an arylsulfonate.

Preferably the hydroxylamine is N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine, N,N-bis(2-hydroxypropyl)hydroxylamine, N,N-bis(3-hydroxypropyl)hydroxylamine, N,N-dioctadecylhydroxylamine, the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine, N,N-dibenzylhydroxylamine, N,N-bis(2-carboxyethyl)hydroxylamine or N,N-bis(benzylthiomethyl)hydroxylamine.

Most preferably, the hydroxylamine is N,N-diethylhydroxylamine, N,N-bis(2-hydroxypropyl)hydroxylamine, N,N-bis(3-hydroxypropyl)hydroxylamine or

N,N-dibenzylhydroxylamine; most especially N,N-diethylhydroxylamine or its citrate salt.

It is shown that the salts of these hydroxylamines are also beneficial in producing the increase in brightness and the resistance to yellowing in pulp or paper still containing lignin.

The effective stabilizing amounts of the hydroxylamine is 0.001 to 5% by weight based on the pulp or paper. Preferably, the effective stabilizing amount is 0.005 to 4% by weight; preferably 0.01 to 4% by weight.

When a coadditive stabilizer is also present, the effective stabilizing amount of the coadditives is also 0.001 to 5% by weight based on the pulp or paper; preferably 0.005 to 3% by weight; most preferably 0.01 to 2% by weight.

The instant compounds may additionally include an effective stabilizing amount of at least one stabilizer selected from the group consisting of the UV absorbers, the polymeric inhibitors, the sulfur containing inhibitors, the phosphorus containing compounds, the nitrones, the benzofuran-2-ones, fluorescent whitening agents, hindered amine hydroxylamines and salts thereof, hindered amine nitroxides and salts thereof, hindered amines and salts thereof and metal chelating agents.

The compositions which also include a UV absorber are especially preferred. The UV absorber is selected from group consisting of the benzotriazoles, the s-triazines, the benzophenones, the α -cyanoacrylates, the oxanilides, the benzoxazinones, the benzoates and the α -alkyl cinnamates.

Preferably, the UV absorber is a benzotriazole, an s-triazine or a benzophenone, most especially a benzotriazole UV absorber or benzophenone UV absorber.

Typical and useful UV absorbers are, for example,

5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3- α -cumyl-5-tert-octylphenyl)-2H-benzotriazole;
2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole-5-sulfonic acid,
sodium salt;
3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamic acid;
12-hydroxy-3,6,9-trioxadodecyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-
hydrocinnamate;
octyl 3-tert-butyl-4-hydroxy-5-(2H-benzotriazol-2-yl)-hydrocinnamate;
4,6-bis(2,4-dimethylphenyl)-2-(4-(3-dodecyloxy*-2-hydroxypropoxy)-2-hydroxy-
phenyl)-s-triazine (*is mixture of C₁₂₋₁₄oxy isomers);
4,6-bis(2,4-dimethylphenyl)-2-(4-octyloxy-2-hydroxyphenyl)-s-triazine;
2,4-dihydroxybenzophenone;
2,2',4,4'-tetrahydroxy-5,5'-disulfobenzophenone, disodium salt;
2-hydroxy-4-octyloxybenzophenone;
2-hydroxy-4-dodecyloxybenzophenone;
2,4-dihydroxybenzophenone-5-sulfonic acid and salts thereof;
2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and salts thereof;
2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-disodium sulfonate; and
3-(2H-benzotriazol-2-yl)-4-hydroxy-5-sec-butylbenzenesulfonic acid, sodium salt
(CIBAFast® W).

Other preferred compositions are those which additionally contain a polymeric inhibitor; preferably poly(ethylene glycol), poly(propylene glycol), poly(butylene glycol) or poly(vinyl pyrrolidone).

Still other preferred compositions wherein the additional stabilizer is a sulfur containing inhibitor; preferably polyethylene glycol dithiolacetate, polypropylene glycol dithiolacetate, polybutylene glycol dithioacetate, 1-thioglycerol, 2-mercaptoethyl ether, 2,2'-thiodiethanol, 2,2'-dithiodiethanol, 2,2'-oxydiethanethiol, ethylene glycol bithioglycolate, 3-mercapto-1,2-propanediol, 2-(2-methoxyethoxy)-ethanethiol, glycol dimercaptoacetate, 3,3'-dithiopropionic acid, polyethylene glycol dithiol, polypropylene glycol dithiol, polybutylene glycol dithiol or ethylene glycol bis(mercaptoacetate).

Other preferred compositions are those wherein the additional stabilizer is a phosphorus containing compound; preferably tris(2,4-di-tert-butylphenyl) phosphite, 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, sodium hydroxymethyl phosphinate, tetrakis(2,4-di-butylphenyl) 4,4'-biphenylenediphosphonite, tris(nonylphenyl) phosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, 2,2'-ethylidenebis(2,4-di-tert-butylphenyl) fluorophosphite or 2-butyl-2-ethylpropan-1,3-diyl 2,4,6-tri-tert-butylphenyl phosphite.

Still other preferred compositions are those wherein the additional stabilizer is a benzofuran-2-one; preferably 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-2H-benzofuran-2-one.

Still other preferred composition are those wherein the additional stabilizer is a metal chelating agent; preferably citric acid, keto acids, gluconates, heptagluconates, phosphates, phosphonates and aminocarboxylic acid chelates, such as ethylenediamine-tetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) and diethylene-triaminepentamethylenephosphonic acid (DTPMPA).

Some preferred compositions contain a mixture of additional stabilizers such as a mixture of a UV absorber and polymeric inhibitor; or a mixture of a UV absorber and a sulfur containing compound; or a mixture of a UV absorber and a phosphorus containing

compound; or a mixture of a UV absorber and a metal chelating agent; or a mixture of a polymeric inhibitor and a sulfur containing compound; or a mixture of a polymeric inhibitor and a phosphorus containing compound; or a mixture of a sulfur containing compound and a phosphorus containing compound; or a mixture of a UV absorber, a polymeric inhibitor and a sulfur containing compound; or a mixture of a UV absorber, a polymeric inhibitor and a phosphorus containing compound; or a mixture of a UV absorber, a polymeric inhibitor, a sulfur containing compound and a phosphorus containing compound; or a mixture of a UV absorber, a polymeric inhibitor and a metal chelating agent.

Some preferred compositions are those wherein the additional stabilizer is a mixture of a hindered amine hydroxylamine or hindered amine hydroxylamine salt with at least one other stabilizer selected from the group consisting of the UV absorbers, the polymeric inhibitors, the sulfur containing inhibitors, the phosphorus containing compounds, fluorescent whitening agents, metal chelating agents and hindered amine nitroxides and salts thereof.

Some preferred composition are those wherein the additional stabilizer is a mixture of a hindered amine hydroxylamine with at least one optical brightener such as 2,2'-[(1,1'-diphenyl)-4,4'-diyl-1,2-ethenediyl]bis-benzenesulfonic, disodium salt {or bis[4,4'-(2-stilbenesulfonic acid)], disodium salt} which is TINOPAL[®] SK, Ciba.

Preferably the compositions are those wherein the compound of formula I, II, III, IA, IIA or IIIA is of low molecular weight or contains hydrophilic moieties or is both of low molecular weight and contains hydrophilic moieties.

The instant invention also pertains to a process for preventing the loss of brightness and for enhancing resistance to yellowing of a pulp or paper, particularly a chemimechanical or thermomechanical pulp or paper which still contain lignin, which comprises

treating said pulp or paper with an effective stabilizing amount of a compound of formula I, II or III, or formula IA, IIA or IIIA as described above.

The instant inhibitor additive system can be added to pulp or paper at a number of places during the manufacturing or processing operations. These include

- a. on a pulp slurry in the latency chest;
- b. on a pulp slurry in or after the bleaching stage in a storage, blending or transfer chest;
- c. on pulp during or after bleaching, washing and dewatering followed by cylinder or flash drying;
- d. before or after the cleaners;
- e. before or after the fan pump to the paper machine headbox;
- f. to the paper machine white water;
- g. to the silo or save all;
- h. in the press section using a size press, coater or spray bar;
- i. in the drying section using a size press, coater or spray bar;
- j. on the calender using a wafer box;
- k. on paper in an off-machine coater or size press; and/or
- l. in the curl control unit.

Clearly, the precise location where the stabilizer additives should be added will depend on the specific equipment involved, the exact process conditions being used and the like. In some cases, the additives may be added at one or more locations for most effectiveness.

If the stabilizer or other coadditives are not themselves "water-soluble", they may be dispersed or emulsified by standard methods prior to application. Alternatively, the stabilizer and/or coadditives may be formulated into a paper sizing or paper coating formulation.

The following examples are for illustrative purposes only and are not to be construed to limit the instant invention in any manner whatsoever.

Handsheet Treatment

All additives are applied by syringe-injecting the appropriate weight % of additive combination in either an aqueous solution when the additive is water soluble, or a solution in 1:1 ethanol/dioxane, onto bleached thermomechanical pulp (BTMP) brightness squares (4 cm x 4cm). The clamped sheets are allowed to air dry for one day.

The brightness of the handsheets is recorded before and after treatment by light exposure under controlled intensity conditions.

Accelerated testing is carried out by subjecting the treated sheets to accelerated light induced yellowing in a fan-cooled light box containing eight fluorescent lamps with a spectral maximum output at 5700 Å with a total output approximately 43 times greater than normal office fluorescent lamps. The lamps are about ten inches away from the handsheets being illuminated.

Ambient testing is carried out by placing the treated handsheets on a desk under normal cool-white fluorescent office lights at a nominal distance of six feet.

In both cases, ISO brightness is tracked as a function of photolysis time and converted to post color number (PC number) in the usual manner.

Post color (PC) number is defined as follows:

$$PC = [(k/s)_{\text{after}} - (k/s)_{\text{before}}] \times 100$$

$$k/s = (1 - R_{\text{inf}})^2 / 2 R_{\text{inf}}$$

where k and s are the absorption and scattering coefficients, respectively, and R_{inf} is the value of ISO brightness.

The relationship between R_{inf} and the chromophore concentration is non-linear, whereas, the PC number is roughly linearly related to the concentration of the chromophore in the sample.

Low PC numbers are desired as they indicate less yellowing.

When, using the ambient test conditions, untreated BTMP handsheets are compared to Kraft handsheets after 60 days, the BTMP handsheets have a PC number which is about 10 while the Kraft paper has a PC number which is about 0.39. The Kraft handsheets are clearly less yellow than untreated BTMP handsheets after exposure to ambient light.

The incident light flux for the accelerated yellowing experiments (Examples 1-10) is 43 times greater than normal office fluorescent lamps as measured by the A. W. Speery SLM-110 digital light power meter. The brightness of the handsheets is tracked and compared to that of untreated sheets exposed in the same manner. The treated sheets exhibit significant resistance to yellowing as is seen below.

Materials Used in the Examples

Compound A is N,N-diethylhydroxylamine.

Compound B is N,N-dibenzylhydroxylamine.

Compound C is N,N-dioctadecylhydroxylamine.

Compound D is the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine.

Compound E is tris(N,N-diethylhydroxylammonium) citrate.

PEO is poly(ethylene glycol) of molecular weight 300.

TINUVIN[®] 328 (Ciba) is 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole.

TINOPAL[®] SK (Ciba) is 2,2'-[(1,1'-diphenyl)-4,4'-diyl-1,2-ethenediyl]bis-benzene-sulfonic, disodium salt {or bis[4,4'-(2-stilbenesulfonic acid)], disodium salt}.

CIBAFast[®] W (Ciba) is 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-sec-butylbenzene-sulfonic acid, sodium salt.

Compound F is N,N-bis(2-carboxyethyl)hydroxylamine.

Compound G is N,N-bis(benzylthiomethyl)hydroxylamine.

Example 1

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 1.0% by weight of N,N-diethylhydroxylamine (Compound A) and exposed to accelerated aging as described above. The treated sheet in exhibits a substantial inhibition of yellowing compared to the untreated control sheet as seen by inspection of the PC numbers given in the table below. Lower PC numbers indicate less color.

<u>Time hours</u>	<u>Compound A PC number</u>	<u>Control PC number</u>
0	0	0
23.6	2.28	5.14
29.4	2.86	6.07
48.7	5.00	9.01
97.8	10.40	15.75
120.3	12.95	18.54
144.0	15.77	21.48
172.2	19.10	24.95

Example 2

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.3% by weight of Compound B and 2.0% by weight of poly(ethylene glycol), molecular weight 300 (PEO). Again, the treated sheet exhibits an excellent resistance to yellowing as compared to the untreated control sheet.

Example 3

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.3% by weight of Compound C and 1.0% by weight of 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole (TINUVIN[®] 328, Ciba). The treated sheet shows surprisingly excellent resistance to yellowing especially in contrast to the untreated control sheet.

Example 4

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.6% by weight of Compound D, 2.0% by weight of poly(ethylene glycol), molecular weight 300 (PEO), and 1.0% by weight of 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole (TINUVIN[®] 328, Ciba). The treated sheet shows extraordinary resistance to yellowing especially in contrast to the untreated control sheet.

Example 5

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.3% by weight of Compound A and 1.0% by weight of TINOPAL[®] SK. Again, the treated sheet exhibits an excellent resistance to yellowing as compared to the untreated control sheet.

Example 6

Accelerated Yellowing with High Intensity Lamps

A BTMP sheet is treated with 0.3% by weight of Compound B and 1.0% by weight of CIBAFast[®] W. The treated sheet shows surprisingly excellent resistance to yellowing especially in contrast to the untreated control sheet.

Example 7

A BTMP sheet is treated with 0.33% and with 0.66% by weight of N,N-diethylhydroxylamine (Compound A) and 0.5% by weight of CIBAFast[®] W and then exposed to accelerated aging as described above. The treated sheet exhibits a substantial inhibition of yellowing compared to the untreated control sheet as seen by inspection of the PC numbers given in the table below. Lower PC numbers indicate less color.

Time in <u>Days</u>	0.5% W 0.66% A <u>PC number</u>	0.5% W 0.33% A <u>PC number</u>	Control <u>PC number</u>
0	0	0	0
0.85	1.18	1.43	2.80
1.84	2.55	2.75	4.71
2.79	3.90	4.24	6.94
3.83	5.46	5.99	8.91
4.75	7.05	7.63	11.03
5.77	8.63	9.23	13.08
6.81	9.92	10.56	14.42
7.75	10.93	11.62	15.57
8.74	11.91	12.53	16.38

Example 8

A BTMP sheet is treated with 0.33% and with 0.66% by weight of tris(N,N-diethylhydroxylammonium) citrate (Compound E) and 0.5% by weight of CIBAFast® W and then exposed to accelerated aging as described above. The treated sheet exhibits a substantial inhibition of yellowing compared to the untreated control sheet as seen by inspection of the PC numbers given in the table below. Lower PC numbers indicate less color.

Time in Days	0.5% W 0.66% E <u>PC number</u>	0.5% W 0.33% E <u>PC number</u>	Control <u>PC number</u>
0	0	0	0
0.85	0.94	1.26	2.80
1.84	2.10	2.54	4.71
2.79	3.43	3.94	6.94
3.83	5.31	5.66	8.91
4.75	6.97	7.03	11.03
5.77	8.43	8.71	13.08
6.81	9.98	10.08	14.42
7.75	10.78	10.96	15.57
8.74	11.91	12.18	16.38

Example 9

A BTMP sheet is treated with 1.0% by weight of N,N-bis(2-carboxyethyl)-hydroxylamine (Compound F) and 1.0% by weight of CIBAFast® W and then exposed to accelerated aging as described above. The treated sheet exhibits a substantial inhibition of yellowing compared to the untreated control sheet.

Example 10

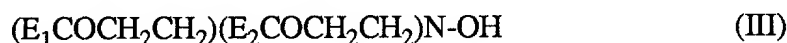
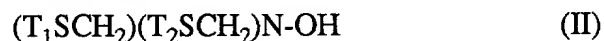
A BTMP sheet is treated with 1.0% by weight of N,N-bis(benzylthiomethyl)-hydroxylamine (Compound G) and 1.0% by weight of CIBAFast® W and then exposed to accelerated aging as described above. The treated sheet exhibits a substantial inhibition of yellowing compared to the untreated control sheet.

WHAT IS CLAIMED IS:

1. A composition having reduced loss of brightness and enhanced resistance to yellowing which comprises

(a) a pulp or paper, and

(b) an effective stabilizing amount of an N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine of formula I, II or III



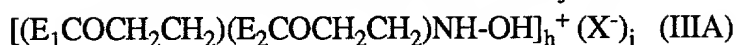
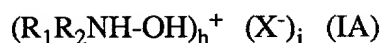
where

R_1 and R_2 are independently alkyl of 1 to 18 carbon atoms, alkyl of 1 to 18 carbon atoms substituted by a hydroxyl group; or benzyl;

T_1 and T_2 are independently alkyl of 1 to 4 carbon atoms, phenyl, 3,5-di-tert-butyl-4-hydroxyphenyl, benzyl or $-CH_2COOH$;

E_1 and E_2 are independently $-OE_3$, $-NHE_3$ or $-NE_3E_4$ where E_3 and E_4 are independently hydrogen, alkyl of 1 to 4 carbon atoms or said alkyl substituted by one hydroxyl group; or

of an acid salt of formula IA, IIA or IIIA



where

R_1 , R_2 , T_1 , T_2 , E_1 and E_2 are as defined above,

X is an inorganic or organic anion, and

the total charge of cations h is equal to the total charge of anions j.

2. A composition according to claim 1 wherein component (a) is a pulp or paper which still contains lignin.

3. A composition according to claim 1 where in the formula IA, IIA or IIIA, X is phosphate, phosphonate, carbonate, bicarbonate, nitrate, chloride, bromide, bisulfite, sulfite, bisulfate, sulfate, borate, formate, acetate, benzoate, citrate, oxalate, tartrate, acrylate, polyacrylate, fumarate, maleate, itaconate, glycolate, gluconate, malate, mandelate, tiglate, ascorbate, polymethacrylate, a carboxylate of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid or of diethylenetriaminepentaacetic acid, a diethylenediaminetetraacetic acid or of diethylene-triaminepentaacetic acid, an alkylsulfonate or an arylsulfonate.

4. A composition according to claim 1 wherein the hydroxylamine of formula I, II or III is N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine, N,N-bis(2-hydroxypropyl)hydroxylamine, N,N-bis(3-hydroxypropyl)hydroxylamine, N,N-di-octadecylhydroxylamine, the N,N-dialkylhydroxylamine product made by the direct oxidation of N,N-di(hydrogenated tallow)amine, N,N-dibenzylhydroxylamine, N,N-bis(2-carboxyethyl)hydroxylamine or N,N-bis(benzylthiomethyl)hydroxylamine.

5. A composition according to claim 4 wherein the hydroxylamine is N,N-diethylhydroxylamine, N,N-bis(2-hydroxypropyl)hydroxylamine, N,N-bis(3-hydroxypropyl)hydroxylamine or N,N-dibenzylhydroxylamine.

6. A composition according to claim 1 wherein the hydroxylamine is N,N-diethylhydroxylamine or its citrate salt.

7. A composition according to claim 1 which additionally includes an effective stabilizing amount of at least one stabilizer selected from the group consisting of the UV absorbers, the polymeric inhibitors, the sulfur containing inhibitors, the phosphorus containing compounds, the nitrones, the benzofuran-2-ones, fluorescent whitening agents, hindered amine hydroxylamines and salts thereof, hindered amine nitroxides and salts thereof, hindered amines and salts thereof and metal chelating agents.

8. A composition according to claim 7 wherein the additional stabilizer is a UV absorber.

9. A composition according to claim 8 wherein the UV absorber is selected from group consisting of the benzotriazoles, the s-triazines, the benzophenones, the α -cyanoacrylates, the oxanilides, the benzoxazinones, the benzoates and the α -alkyl cinnamates.

10. A composition according to claim 8 wherein the UV absorber is a benzotriazole, an s-triazine or a benzophenone.

11. A composition according to claim 10 wherein the UV absorber is 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-sec-butylbenzene sulfonic acid, sodium salt (CIBAFast® W).

12. A composition according to claim 7 wherein the additional stabilizer is a polymeric inhibitor.

13. A composition according to claim 12 wherein the polymeric inhibitor is poly(ethylene glycol), poly(propylene glycol), poly(butylene glycol) or poly(vinyl pyrrolidone).

14. A composition according to claim 7 wherein the additional stabilizer is a sulfur containing inhibitor.

15. A composition according to claim 14 wherein the sulfur containing inhibitor is polyethylene glycol dithiolacetate, polypropylene glycol dithiolacetate, polybutylene glycol dithioacetate, 1-thioglycerol, 2-mercaptoethyl ether, 2,2'-thiodiethanol, 2,2'-dithiodiethanol, 2,2'-oxydiethanethiol, ethylene glycol bithioglycolate, 3-mercapto-1,2-propanediol, 2-(2-methoxyethoxy)-ethanethiol, glycol dimercaptoacetate, 3,3'-dithiopropionic acid, polyethylene glycol dithiol, polypropylene glycol dithiol, polybutylene glycol dithiol or ethylene glycol bis(mercaptoacetate).

16. A composition according to claim 7 wherein the additional stabilizer is a phosphorus containing compound.

17. A composition according to claim 16 wherein the phosphorus containing compound is tris(2,4-di-tert-butylphenyl) phosphite, 2,2',2''-nitrilo[triethyl-tris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], tris(2,4-di-tert-butyl-6-ethylphenyl) phosphite, sodium hydroxymethyl phosphinate, tetrakis(2,4-di-butylphenyl) 4,4'-biphenylenediphosphonite, tris(nonylphenyl) phosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, 2,2'-ethylidenebis(2,4-di-tert-butylphenyl) fluorophosphite or 2-butyl-2-ethylpropan-1,3-diyl 2,4,6-tri-tert-butylphenyl phosphite.

18. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and polymeric inhibitor.

19. A composition according to claim 7 wherein the additional stabilizer is a

mixture of a UV absorber and a sulfur containing compound.

20. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and a phosphorus containing compound.

21. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and a metal chelating agent.

22. A composition according to claim 7 wherein the additional stabilizer is a mixture of a polymeric inhibitor and a sulfur containing compound.

23. A composition according to claim 7 wherein the additional stabilizer is a mixture of a polymeric inhibitor and a phosphorus containing compound.

24. A composition according to claim 7 wherein the additional stabilizer is a mixture of a sulfur containing compound and a phosphorus containing compound.

25. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber, a polymeric inhibitor and a sulfur containing compound.

26. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber, a polymeric inhibitor and a phosphorus containing compound.

27. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber, a polymeric inhibitor and a metal chelating agent.

28. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber, a polymeric inhibitor, a sulfur containing compound and a phosphorus containing compound.

29. A composition according to claim 7 wherein the additional stabilizer is a

mixture of a UV absorber and a hindered amine nitroxide.

30. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and a hindered amine hydroxylamine.

31. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and a hindered amine hydroxylamine salt.

32. A composition according to claim 7 wherein the additional stabilizer is a mixture of a UV absorber and a hindered amine.

33. A composition according to claim 7 wherein the additional stabilizer is a fluorescent whitening agent.

34. A composition according to claim 33 wherein the fluorescent whitening agent is 2,2'-[(1,1'-diphenyl)-4,4'-diyl-1,2-ethenediyl]bis-benzenesulfonic, disodium salt {or bis[4,4'-(2-stilbenesulfonic acid)], disodium salt} (TINOPAL[®] SK).

35. A composition according to claim 1 wherein the effective stabilizing amount of the hydroxylamine or hydroxylamine salt is 0.001 to 5% by weight based on the pulp or paper.

36. A composition according to claim 1 wherein the effective stabilizing amount of the hydroxylamine is 0.005 to 4% based on the pulp or paper.

37. A composition according to claim 1 wherein the effective stabilizing amount of the hydroxylamine is 0.01 to 4% based on the pulp or paper.

38. A composition according to claim 7 wherein the effective stabilizing amount of a coadditive is 0.001 to 5% by weight based on the pulp or paper.

39. A composition according to claim 7 wherein the effective stabilizing amount of a coadditive is 0.005 to 3% by weight based on the pulp or paper.

40. A composition according to claim 7 wherein the effective stabilizing amount of a coadditive is 0.01 to 2% based on the pulp or paper.

41. A process for preventing the loss of brightness and for enhancing resistance to yellowing of pulp or paper which comprises

treating said pulp or paper with an effective stabilizing amount of a hydroxylamine compound of formula I, II or III or hydroxylamine salt of formula IA, IIA or IIIA according to claim 1.

42. A process according to claim 41 wherein the pulp or paper still contains lignin.

43. A process according to claim 40 wherein the hydroxylamine is N,N-diethylhydroxylamine or its citrate salt.

A-21835/P2/CGC 2002

INHIBITION OF PULP AND PAPER YELLOWING
USING HYDROXYLAMINES AND OTHER COADDITIVES

Abstract of the Disclosure

Pulps or papers, especially chemimechanical or thermomechanical pulps or papers, which still contain lignin, have enhanced resistance to yellowing when they contain an effective stabilizing amount of a N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine or an ammonium salt thereof. This performance is often further enhanced by the presence of one or more coadditives selected from the group consisting of the UV absorbers, the polymeric inhibitors, the nitrones, the fluorescent whitening agents and metal chelating agents. Combinations of hydroxylamines or their salts, benzotriazole or benzophenone UV absorbers and a metal chelating agent are particularly effective. N,N-Diethylhydroxylamine and N,N-dibenzylhydroxylamine and their acid salts are surprisingly effective for this purpose.

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☒ Original ☐ Supplemental ☐ Substitute ☐ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

INHIBITION OF PULP AND PAPER YELLOWING USING
HYDROXYLAMINES AND OTHER COADDITIVES

which is described and claimed in:

- ☐ the attached specification.
- ☒ the specification in U.S. application No. _____
filed _____, and as amended on _____ (if applicable).
(month/day/year) (month/day/year)
- ☐ the specification in International Application No. PCT/ _____,
filed _____, assigned U.S. Application No. _____ (if applicable), and as amended
(month/day/year)
- ☐ under PCT Article 19 on _____ (if applicable)
(month/day/year)
- ☐ under PCT Article 34 on _____ (if applicable)
(month/day/year)
- ☐ and further amended on _____ (if applicable)
(month/day/year)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

COUNTRY/REGION (OR PCT)	APPLICATION NO.	FILING DATE (month/day/year)	PRIORITY CLAIMED	
_____	_____	_____	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes	<input type="checkbox"/> No

I hereby claim the benefit under 35 USC § 119(e) of any United States provisional application(s) listed below:

APPLICATION NO.	FILING DATE (month/day/year)
_____	_____
_____	_____
_____	_____

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. APPLICATION NO.	FILING DATE (month/day/year)	STATUS
<u>09/177,016</u>	<u>October 22, 1998</u>	<input type="checkbox"/> Patented <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Abandoned

_____	_____	<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
_____	_____	<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
PCT APPLICATION NO.	INTERNATIONAL FILING DATE (month/day/year)	U.S. APPLICATION NO. (if any)	STATUS	
_____	_____	_____	<input type="checkbox"/> Patented	
_____	_____	_____	<input type="checkbox"/> Pending	
_____	_____	_____	<input type="checkbox"/> Abandoned	

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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